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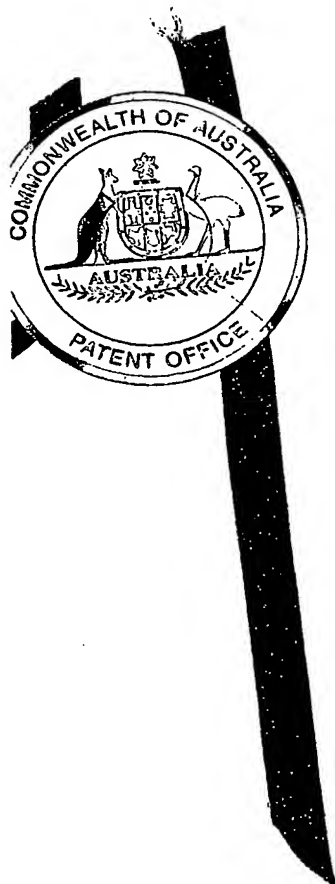
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in connection with Application No. 2002951339 for a patent by GRIFFITH
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AUSTRALIA
Patents Act 1990

PROVISIONAL SPECIFICATION

2002 **filed 12th September 2002**

Invention Title : Non Volatile Memory Cell

Applicant: Griffith University

**Inventors: H Barry Harrison
 Sima Dimitrijevic**

The invention is described in the following statement:

NON VOLATILE MEMORY CELL

This invention relates to a nonvolatile memory cell and in particular to a silicon carbide based memory cell.

Background to the invention

- 5 Random Access Memory devices are volatile in that power is needed to retain data indefinitely as compared to non volatile storage.

Flash memory provides the complementary functions in modern electronic systems. Flash memory uses a floating gate which is charged or discharged to change the logic state. The charge and discharge times are finite and the
10 discharge is relatively slow. It is a read-only memory (ROM), because the information writing takes too long and is limited to a certain number of writing cycles, so it cannot be used for RAM applications. However, it provides a nonvolatile storage of the information, which is kept even when any power is disconnected from the memory cells. Flash memory is also dependent on
15 processing and in practice there is a need to adjust for processing by having a micro processor on the same chip with built in corrections.

There have been attempts to form non volatile random access memory (NVRAM) devices - a memory cell with access characteristics of silicon RAMs and with retention times of silicon ROMs (flash memories) - and USA patent 6373095 is an
20 example.

Another challenge in developing memory devices is to reduce the feature size currently at $8F^2$. F is the *minimum feature* (the minimum line width that can be achieved by a certain technology), and $8F^2$ shows that the structure of state-of-the-art memory cells is such that every cell takes an area of $8F^2$. This challenge
25 has been outlined by S.Okhonin, M. Nagoga, J.M. Sallese and P Fazan (IEEE Electron Device letters Vol 23 No 2 Feb 2002). A limiting factor in down scaling feature size in silicon is that memory capacitance is dependent on F .

Silicon Carbide is not widely used to produce semiconductor devices which are
30 mostly fabricated in silicon. Silicon carbide has been proposed for use in transistors but not for memory devices in USA patents 5831288, 6218254, and 6281521.

USA patent 6365919 discloses a Silicon carbide junction field effect transistor (JFET) USA patent 5465249 discloses a silicon carbide NVRAM cell which incorporates a transistor and capacitor in silicon carbide.

5 USA patents 5801401, 5989958 and 6166401 disclose a memory device using a silicon carbide floating gate.

It is an object of this invention to provide a NVRAM that is capable of having a small feature size and avoids the disadvantages of flash memory. A further object is to provide a cell that can enable more aggressive down scaling and
10 significant reductions in power dissipation. This of course will also increase the density of memory storage.

Brief description of the invention

To this end the present invention provides a NVRAM which includes a silicon
15 carbide transistor in which the gate oxide is formed in the presence of N_2O .

This invention provides a silicon carbide transistor in which the mechanisms of electron-hole recombination (both, bulk and surface), as well as charge leakage, are reduced to levels that allow a non-equilibrium state to be maintained for very long periods of time.

20 This invention is partly predicated on the realisation that nitrided oxide in the $SiO_2 - SiC$ interface results in long charge retention times that makes it suitable for non volatile memory storage devices. The process of preparing the device is based on *nitridation* of the $SiC-SiO_2$ interface, either by a direct oxide growth (in) or oxide annealing in either NO or N_2O ambients.

25 In a further aspect of this invention there is provided a metal oxide semiconductor field effect transistor (MOSFET) implemented in silicon carbide with the bit lines (the MOSFET drains) crossing the word lines (the MOSFET sources) and the gates are in parallel with the word lines. This MOSFET can be used as a single transistor (capacitor less) NVRAM cell.

30 This structure has a feature size of $4 F^2$. Another advantage is that the logic levels are implemented as two states of channel resistance due to the silicon carbide charge retention and that the difference in the resistance values of the

two levels is not critically dependent on F. A further advantage is multi level logic which is bought about by different amounts of gate charge and thus multiple levels of resistance.

5 Compared to Flash memory lower voltages are required and the speed of charging and discharging is greater than with Flash. The memory cell of this invention has none of the disadvantages of Flash memory with the added benefit that the cell may have several (infinite) logic states if they are needed.

This aspect of the invention is predicated on the development of a fabrication method which results in a self aligned MOSFET. The method includes the
10 essential step of forming a nitrided silicon oxide gate on the silicon carbide substrate and subsequently carrying out the ion implantation and then finishing the formation of the MOSFET.

The development of a fabrication method which results in a self aligned MOSFET with a metal gate provides performance improvements (better down scaling of F, reduced power consumption, and reduced leakage through the gate oxide). Self-aligned MOSFETs are routinely made in silicon (either with polysilicon or metal gates). The challenge in SiC is due to the need for high-temperature annealing to activate the doping of the drain and the source areas after creating them by ion implantation with the MOSFET gates as self-aligning masks. The ion implantation
20 may be performed at room temperature, but this requires prohibitively high annealing temperatures ($>1400^{\circ}\text{C}$). An alternative method is to perform the ion-implantation at high temperatures (about 800°C), in which case the post implant annealing temperature up to 1300°C is sufficient. The challenge with this is to find a metal (or a metal-based structure) that will provide the necessary adhesion to
25 the gate oxide and that will withstand the high-temperature ion implantation. A preferred metal is Molybdenum and this allows a Mo-gate process that satisfies the conditions for fabrication of self-aligned SiC MOSFETs by hot ion implantation. Other suitable materials are P^+ polysilicon, and platinum silicide. An essential feature of this preferred method is the use of a capping dielectric
30 (deposited oxide, for example) to prevent sublimation of the Mo gate, as well as coating the capping dielectric by a thin metal film to avoid damaging charging effects during the ion implantation.

The Structure created by this fabrication structure creates a transistor with at least two states of its channel resistance — one of the states is the equilibrium state and the others are non-equilibrium state that retains charge so that the MOSFET can be used as a nonvolatile memory cell.

5

Detailed description of the invention

Preferred embodiments of the invention will be described with reference to the drawings in which

- Figure 1 is cross sectional view of a memory cell of this invention;
- 10 Figure 2 is a top view of the cell of figure 1;
- Figure 3 illustrates the reading states of the cell of this invention;
- Figure 4 illustrates the writing of logic 0;
- Figure 5 illustrates the writing of logic 1;
- Figure 6 illustrates step 1 of a fabrication method applicable to this invention;
- 15 Figure 7 illustrates step 2 of a fabrication method applicable to this invention;
- Figure 8 illustrates step 3 of a fabrication method applicable to this invention;
- Figure 9 illustrates step 4 of a fabrication method applicable to this invention;
- Figure 10 illustrates step 5 of a fabrication method applicable to this invention;
- Figure 11 illustrates step 6 of a fabrication method applicable to this invention;
- 20 Figure 12 illustrates step 8 of a fabrication method applicable to this invention;

Technological Considerations

- The critical technological aspects, in terms of proper functioning of the memory cell of this invention, are limited to the issues of (1) low recombination rate and
- 25 (2) low leakage through the gate oxide. The requirement for low recombination rate is the reason why silicon cannot be used to achieve very long storage times. Many semiconductor materials with wide energy gaps can theoretically fulfill this requirement, at least as far as the bulk recombination rate is concerned.
- However, the difficulty lies in achieving a high quality interface between the
- 30 semiconductor with wide energy gap and a dielectric, so that the surface recombination rate is sufficiently reduced. The native oxide of SiC is silicon-dioxide, the same dielectric as in the only industry-standard semiconductor-

dielectric interface developed so far — the silicon-silicon dioxide interface. SiC is the only wide energy gap material that can provide a high-quality interface with its native dielectric, so the implementation of the memory cell of this invention, is practically limited to silicon carbide substrate. There are many SiC polytypes (3C, 4H, 6H,...) and each of them would satisfy the essential requirements. The energy gap of 3C SiC is about 2.4 eV, which is a smaller value compared to the other common polytypes (about 3.0 eV for 6H and about 3.2 eV for 4H SiC). This means the recombination rate will be the largest of all common polytypes. However, a good-quality 3C material with a good quality gate-dielectric interface can provide a low enough recombination rate for the implementation of the nonvolatile RAM cell. The attractiveness of 3C SiC is that it can be deposited on Si, enabling integration of the nonvolatile RAM with state-of-the-art complementary electronics and with the mature technology processes developed for silicon.

The quality of the interface between SiC and the gate dielectric is essential for both requirements (low surface recombination rate and low leakage through the gate dielectric). This invention provides a specific treatment of the interface between SiC and the gate dielectric as one means of achieving the required high-quality interface. This treatment results in "nitrided" interface, where nitrogen atoms remove and passivate interfacial defects. The interface nitridation can be achieved by either direct oxide growth or by annealing of pre-grown oxide in either NO or N₂O ambients at high temperatures (>1000°C).

The memory cell of this invention stores minority carriers in the MOSFET channel (holes in the case of P-channel MOSFET on N-type substrate). The recombination rate of the minority carriers in the channel is low when the SiC surface is depleted or inverted, but not when the surface is in accumulation. Therefore, it is preferable to select the gate material so that the surface is not inverted at $V_G = 0V$. In other words, it is preferable to select the gate material so that the flat-band voltage (V_{FB}) is positive for a P-channel MOSFET. The flat-band voltage is given by

$$V_{FB} = \phi_{ms} - q N_{OC}/C_{ox}$$

where ϕ_{ms} is the work-function difference, N_{oc} is the density of the effective gate-oxide charge, and C_{ox} is the gate-oxide capacitance. In the case of N-type 4H SiC (P-channel MOSFETs), the condition for a positive flat-band voltage is satisfied
 5 by the most suitable gate materials. For example, the work-function differences are about 0.5 eV, 1.2 eV, and 1.8 eV for molybdenum, P⁺ polysilicon, and platinum silicide, respectively. In the case of N-type 3C Si, the work-function differences are about -0.4 eV, 0.3 eV, and 0.8 eV for molybdenum, P⁺ polysilicon, and platinum silicide, respectively. Given that the shift due to the effective oxide
 10 charge is usually negative ($-q N_{oc}/C_{ox} < 0$), the preferred material in the case of 3C SiC is platinum silicide.

To reduce the surface recombination rate, the gate leakage, and the minimum feature (F), the preferred implementation of the MOSFET in this invention is as a self-aligned structure (self-aligned gate and source/drain regions). Self-aligned
 15 MOSFETs have been made in silicon (either with polysilicon or metal gates). The challenge in SiC is due to the need for high-temperature annealing to activate the doping of the drain and the source areas after creating them by ion implantation with the MOSFET gates as self-aligning masks. The ion implantation can be performed at room temperature, but this requires prohibitively high annealing
 20 temperatures ($>1400^{\circ}\text{C}$). An alternative method is to perform the ion-implantation at high temperatures (about 800°C), in which case the post implant annealing temperature up to 1300°C is sufficient. Gate materials that satisfy this criterion include polysilicon, molybdenum, and platinum silicides.

25 A preferred memory cell is shown schematically in figures 1 and 2. The cell topology is a capacitor-less 1T-DRAM cell. Fig. 1 shows the cross-section and Fig. 2 shows the top view. Technologically, the cell is an ordinary *metal-oxide-semiconductor field-effect transistor (MOSFET)*, implemented in SiC. The SiC film that is needed can be deposited on Si to allow an integration
 30 with today's Si electronics. As shown in Fig. 2, the bit lines (drains of the MOSFETs) cross the word lines (sources of the MOSFETs). The gates of the

MOSFETs (labeled by G) run in parallel with the word lines (sources of the MOSFETs). This corresponds to a cell area of $4F^2$.

Fig. 1 illustrates the implementation with P-channel MOSFETs [current experimental results suggest lower recombination rates and leakage when the gate oxide (gate dielectric) is grown on N-type SiC (N substrate in Fig. 1)]. Further, a specific suggestion is to select the gate material so that the flat-band voltage $V_{FB} > 0$ and the threshold voltage $V_T < 0$. With this, the channel area is depleted for $V_G = 0$. Some negative charge exists in the gate to compensate the positive donor ions in the depleted SiC surface, but this equilibrium charge will be neglected in the following considerations (for clarity).

Information Reading

The equilibrium state (depleted surface) corresponds to a very high channel resistance and is defined as logic '0' (Fig. 3a). The reading of this state is achieved by connecting the word line to ground and the bit line to a small negative voltage (V_B). The channel-resistance at the cross between the word and the bit lines determines the current, and if this MOSFET has a depleted channel, there is no current (logic '0').

The logic '1' state is achieved by trapping extra negative charge in the floating gate to reduce the potential in the channel sufficiently so that the inversion layer of holes is formed at the SiC surface (Fig. 3b). Reading is the same, with a difference that the response is a significant current through the channel (logic '1'). Note that the application of voltage to the drains and the grounding of the sources does not affect the stored information. There will be a small alteration of the surface potential, but the charge in the floating gate will not change, so the surface SiC condition will be restored after the reading cycle.

Storage Time

The logic '1' state is nonequilibrium, so the natural mechanisms will act to remove the inversion-layer holes to bring the structure into equilibrium. There are two possible mechanisms of hole removal: (1) leakage through the gate oxide (gate dielectric), and (2) hole-electron recombination. A high-quality oxide-SiC interface can be achieved to reduce the leakage to sufficient levels. experimental

results indicate that sufficiently low surface-recombination levels are possible as well.

Connecting the Floating Gate for the Writing Operations

Writing operations (for both, logic '1' and logic '0') are performed with grounded gates. This is an important aspect of the innovation. The gates do not need to be disconnected from the ground to maintain the non-equilibrium state(s). Therefore, the use of "floating" gates in this invention is quite different from the use of floating gates in today's flash memories (ROMs). In this invention, the gates are disconnected from ground to enable straightforward selection of a cell for information reading and writing. It has been already described that the trapped charge in the floating gate restores the state of the cell after the disturbance caused by the V_B potential used for information reading. Likewise, the state of a cell is not altered when a bit line (MOSFET drains) is connected to a potential for the purpose of information writing, as will be described in the following text. At this point, it is important to stress that the implementation of the switch that disconnects the gates from the ground is not a big issue, given that most of the time the voltage across the switch is equal to zero. This changes only during information reading and writing, which are very short time intervals.

Notwithstanding this, the switch connecting the gates can be implemented as a SiC MOSFET that can maintain a voltage drop (reverse bias across its drain-to-substrate junction) for a very long time due to the very low generation rate.

Writing Logic '0'

Logic '0' corresponds to the equilibrium state (depleted surface). To set this state, the gate line along a selected word line is grounded (Fig. 4). Importantly, this does not change the state of any of the connected MOSFETs that may be in logic '1' state, as the logic '1' states were also written with the gates grounded. After this, the corresponding bit line is grounded, closing a ground-to-ground circuit through the gate-channel capacitance of the MOSFET in the cross between the word and the gate lines. This removes the holes from the channel.

Writing Logic '1'

Again, the gate line along a selected word line is grounded first. In this case, however, the word line (sources) is not left disconnected, but is connected to a

positive voltage that is just below the forward-bias voltage of the source-substrate P-N junction. This leads to a small increase in the density of electrons in the gate, but there should be no injection of holes by the source, so that the original state of the depleted surface is restored in the logic '0' MOSFETs that are not selected by the bit line (drains disconnected). A sufficiently large negative voltage is applied to the selected bit line (MOSFET drains) so that source-substrate P-N junction of the selected MOSFET is set in forward-bias mode and a current of holes flows through the channel. As these holes induce electrons in the gate (Fig. 5), the gate is disconnected to trap the electrons (the situation of a floating gate charged with extra electrons).

N-Channel Inversion Type Self-aligned MOSFET Fabrication Steps:

The following describe in detail the fabrication processes for n-channel inversion type self-aligned MOSFET.

- 15 1] *Define Active Region:* see figure 6
 - 1.1. Clean wafer
 - 1.2. Sputtered 500-nm thick field oxide - SiO_2 [3 hrs = 1.1 μm]
 - 1.3. Deposit photoresist & soft bake
 - 1.4. Expose UV (mask 1)
 - 20 1.5. Develop photoresist & hard bake
 - 1.6. Etch field oxide with BHF
 - 1.7. Remove photoresist by ethanol
- 25 2] *Grown Gate Oxide:* see figure 7
 - 2.1. Clean wafer (without HF)***
 - 2.2. Thermally grown 50 nm gate oxide (nitrided oxide)
[1hr NO, 4hrO₂, 2hrNO, and cool down overnight]
- 30 3] *Formation of Metal Contact Layer for Gate Oxide:* see figure 8
 - 3.1. Sputtered 1- μm thick Mo [200W for 55 min]
 - 3.2. Deposit 200 nm SiO_2 by spin-on-glass (sog) [4000rpm]
 - 3.3. Soft bake @ 200°C for 1 hr

- 3.4. Hard bake @ 900°C for 20 min.
- 3.5. Cool down to 700°C
- 3.6. Deposit photoresist & soft bake
- 3.7. Expose UV (mask 2)
- 5 3.8. Develop photoresist & hard bake
- 3.9. Etch SiO₂ (spin-on-glass) with BHF
- 3.10. Etch Mo [1 min 15s can etch 1-um thick Mo]

- 10 4] *Ion Implantation (N⁺): see figure 9*

- 5] *Activate & Drive-in implanted ion: see figure 10*
 - 5.1. Annealing at 950°C (or 1300°C) for 30 min

- 6] *Open Source/Drain windows: see figure 11*
 - 15 6.1. Spin-on-glass, SiO_{2(Mo)} (to protect Mo sidewall from Ni etchant)
 - 6.2. Deposit photoresist & soft bake
 - 6.3. Expose UV (mask 3)
 - 6.4. Develop photoresist & hard bake
 - 6.5. Etch SiO₂ (SiO_{2(Mo)}, spin-on-glass on MOS-C, MOSFET, and R_c test
 - 20 structure & nitrided oxide on R_c test structure) with BHF
 - 6.6. Remove photoresist by etanol

- 7] *Prepare Bulk Contact Area:*
 - 7.1. Deposit photoresist & soft bake
 - 25 7.2. Expose UV (mask 4)
 - 7.3. Develop photoresist & hard bake
 - 7.4. Etch Mo
 - 7.5. Etch nitrided oxide

- 30 8] *Metallization of Source/Drain/Bulk contact: see figure 12*
 - 8.1. Sputtered 500 nm Ni (time = 40min @ 200°C)
 - 8.2. Deposit photoresist & soft bake

- 8.3. Expose UV (mask 5)
- 8.4. Develop photoresist & hard bake
- 8.5. Etch Ni [Al etchant]
- 8.6. Remove photoresist

5

In summary, the present invention exploits low bulk and surface *recombination* rates that can be achieved in SiC. This fact is utilized to propose a nonvolatile dynamic random-access memory (DRAM) with the following features:

- 10 1. Practically indefinite information storage, even when no power is connected to the cell (memory).
2. Fast reading and writing — comparable to today's DRAMs on silicon that need refreshing (volatile DRAMs).
3. Indefinite number of writing cycles.
- 15 4. A smaller cell size than today's commercial volatile DRAMs — $4F^2$, where F is the minimum feature size.
5. Easier downscaling of F compared to today's volatile DRAMs. This is due to the following factors: (1) the '0' and '1' logic levels are implemented as two states of a channel resistance, so the difference between the two levels does not critically depend on how small F is (as opposed to this, a relatively small
- 20 difference in two capacitance levels is used in today's volatile DRAMs, so that downscaling of the memory capacitor is already a limiting factor); (2) lack of any diffusion in SiC removes the most significant fabrication issues related to channel-length downscaling.
6. Reduced power dissipation.
- 25 7. Multiple logic levels and therefore the chance of higher storage densities.
8. Full compatibility with silicon enable support electronics to be produced in this more mature material.
9. The higher thermal conductivity will also enable higher mass storage of digital information.etc.

30

Those skilled in the art will realize that the invention can be implemented in a variety of ways in a number of configurations without departing from the the critical teaching of this invention.

CLAIMS

1. NVRAM which includes a silicon carbide transistor in which the gate oxide is prepared by direct oxide growth or by annealing of pre-grown oxide in the presence of NO or N₂O.
- 5 2. A metal oxide semiconductor field effect transistor (MOSFET) implemented in silicon carbide with the bit lines (the MOSFET drains) crossing the word lines (the MOSFET sources) and the gates are in parallel with the word lines.
- 10 3. A MOSFET as claimed in claim 2 in which writing operations are performed with grounded gates.
4. A method of fabricating an NVRAM as claimed in claim 1 or a MOSFET as claimed in claim 2 which includes the step of forming a nitrided silicon oxide gate on the silicon carbide substrate and subsequently carrying out the ion implantation and then finishing the formation of the MOSFET.
- 15 5. NVRAM as claimed in claim 1 in which the transistor includes a gate and the gate material is selected from molybdenum, P⁺ polysilicon, and platinum silicide.
- 20 5. NVRAM in which the electron-hole recombination rate and charge leakage are reduced so much that a non-equilibrium charge can be maintained for substantial periods of time, which includes a silicon carbide transistor .

ABSTRACT

A non volatile random access memory cell is formed in silicon carbide and the gate oxide is formed or annealed in the presence of nitrogen. The memory cell comprises a metal oxide semiconductor field effect transistor (MOSFET) implemented in silicon carbide with the bit lines (the MOSFET drains) crossing the word lines (the MOSFET sources) and the gates are in parallel with the word lines. The gate of the MOSFET acts to store charge and thus dictate the "logical" state of the device. The fabrication method includes the step of forming a nitrided silicon oxide gate on the silicon carbide substrate and subsequently carrying out the ion implantation and then finishing the formation of a self aligned MOSFET.

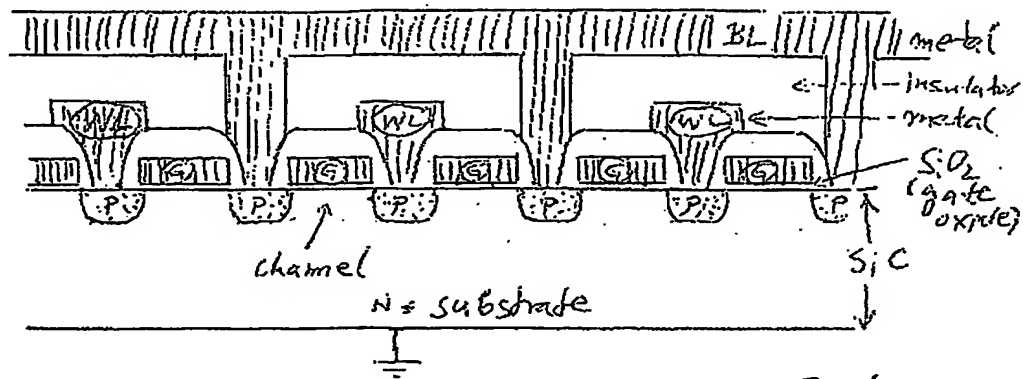


Fig. 1

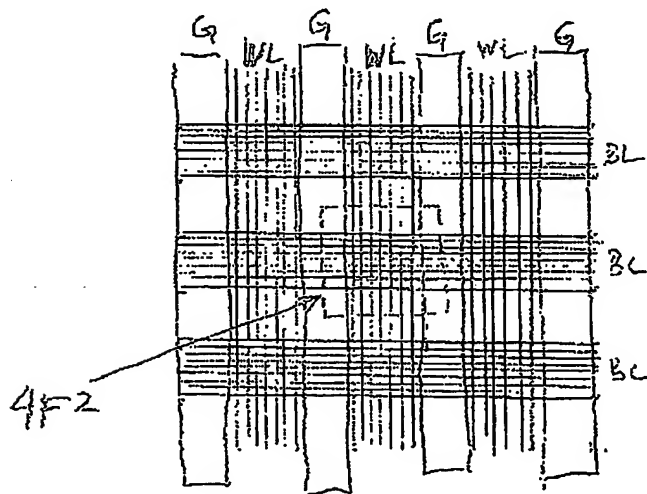


Fig. 2

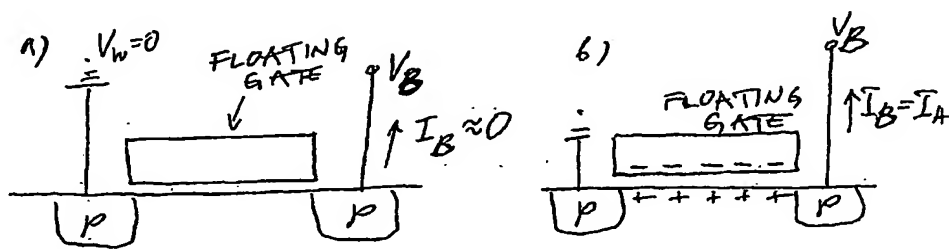


Fig. 3 Reading logic "0" (a)
and logic "1" (b)

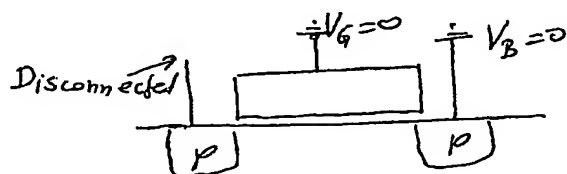


Fig. 4 Writing "0"

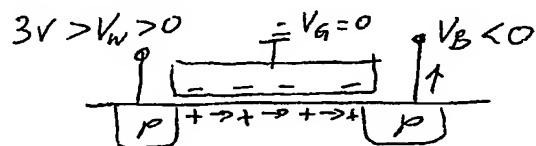


Fig. 5 Writing "1"

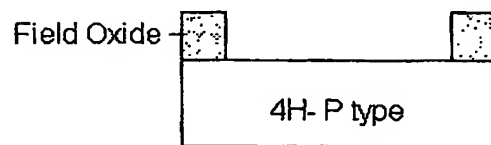
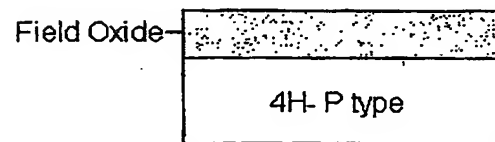


FIGURE 6

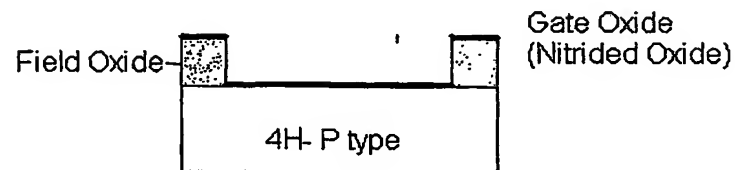


FIGURE 7

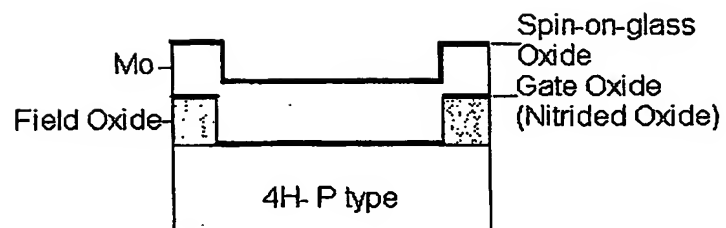


FIGURE 8

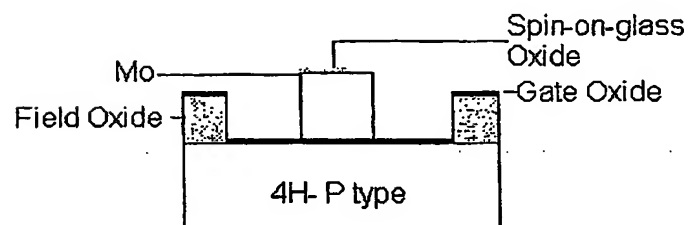


FIGURE 9

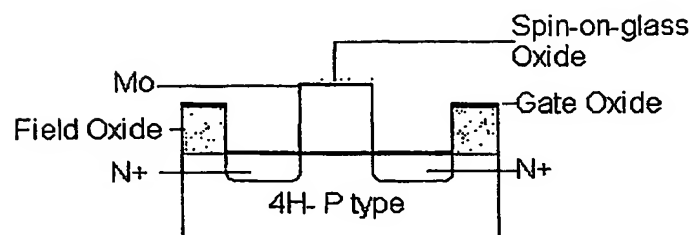


FIGURE 10

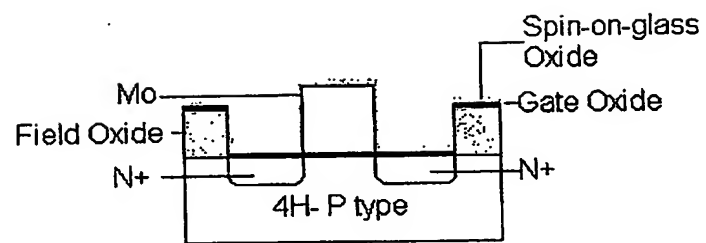


FIGURE 11

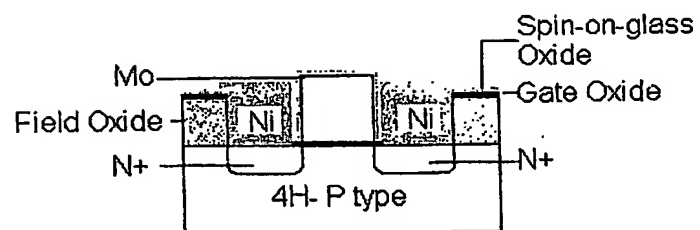


FIGURE 12

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